Interacting Growth Walk on a honeycomb lattice

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(February 1, 2008)

The Interacting Growth Walk (IGW) is a kinetic algorithm proposed recently for generating long, compact, self avoiding walks. The growth process in IGW is tuned by the so called growth temperature $T' = 1/(k_B\beta')$. On a square lattice and at $T' = 0$, IGW is attrition free and hence grows indefinitely. In this paper we consider IGW on a honeycomb lattice. We take contact energy, see text, as $\epsilon = -|\epsilon| = -1$. We show that IGW at $\beta' = \infty$ ($T' = 0$) is identical to Interacting Self Avoiding Walk (ISAW) at $\beta = \ln 4$ ($k_BT = 1/\ln 4 = 0.7213$). Also IGW at $\beta' = 0$ ($T' = \infty$) corresponds to ISAW at $\beta = \ln 2$ ($k_BT = 1/ln2 = 1.4427$). For other temperatures we need to introduce a statistical weight factor to a walk of the IGW ensemble to make correspondence with the ISAW ensemble.

We shall be concerned with a linear homo polymer chain, modelled by a lattice Self Avoiding Walk (SAW). Let z denote the coordination number of the lattice. An ensemble of SAW is generated by the following simple non-reversing blind ant algorithm. A blind ant starts at a site, say origin. The ant steps into one of the z nearest neighbour sites with a probability $p = 1/z$. Since the ant never reverses its step, in the second and subsequent steps, it moves to one of the $z-1$ nearest neighbour sites with a probability $(z-1)^{-1}$. If the ant finds that the site has been visited earlier, then the walk is terminated and we start all over again. Sample loss due to violation of self avoidance is called the problem of attrition because of which growing of large number of long polymer chains becomes difficult. Thus, a walk having N step is generated with a probability given by,

$$\mathcal{P}_N^{\rm SAW}(\mathcal{C}) = \frac{1}{z}\left(\frac{1}{z-1}\right)^{N-1}. \qquad (1)$$

The important point is that as per the above non-reversing blind ant algorithm, all the N step SAWs are generated with the same probability. Note that the only interaction present is due to the excluded volume effect (the hard core repulsion). In the random walk model this is taken care of by the self avoidance condition.

Let us now switch on a weak interaction. The aim is to model the interaction that ensues when a segment of the polymer chain comes close to another segment. The segment - segment interaction can be attractive or repulsive depending on the nature of the monomers present in the polymer chain. This interaction is usually modelled, see for *e.g.* [1] as follows. We say that in an SAW configuration, every pair of occupied nearest neighbour sites but not adjacent along the walk, carries an energy ϵ. We call such a pair, as giving rise to a single non-bonded nearest neighbour (nbNN) contact. If $\epsilon < 0$ then the interaction is attractive and if $\epsilon > 0$, it is repulsive. Thus a walk $\mathcal{C}$ belonging to the SAW ensemble has an energy $E(\mathcal{C}) = n_{NN}(\mathcal{C}) \times \epsilon$, where $n_{NN}(\mathcal{C})$ denotes the total number of nbNN contacts present in $\mathcal{C}$.

The probability with which an SAW would be found in a canonical ensemble of Interacting Self Avoiding Walks (ISAW) at temperature $T = 1/[k_B\beta]$ can now be expressed as,

$$\mathcal{P}_N^{\rm ISAW}(\mathcal{C}) = \frac{\exp\left[-\beta E(\mathcal{C})\right]}{Q(\beta, N)}. \qquad (2)$$

In the above, the denominator is the canonical partition function, given by,

$$Q(\beta, N) = \sum_{\mathcal{C}} \exp\left[-\beta E(\mathcal{C})\right], \qquad (3)$$

from which all the required macroscopic properties of the polymers can be calculated either analytically or numerically, in the thermodynamic limit of $N \to \infty$. In what follows, we consider only attractive interaction, representing weak Van der Walls forces and set $\epsilon = -|\epsilon|$, see for *e.g.* [2] and without loss of generality take the strength of interaction as unity, *i.e.* $|\epsilon| = 1$.

At very high temperatures, $T \to \infty$ ($\beta \to 0$) the nbNN contact interactions are unimportant; a polymer configuration is completely determined by the excluded volume repulsion (present always and taken care of by the self avoidance condition) and entropy. We get a relatively extended configuration representing a polymer under good solvent conditions [3]. As T is lowered, the contact interactions become more and more important and below a critical temperature, called the theta point, there is an abrupt transition to a collapsed phase. At the theta point itself, we get an intermediate phase called the theta polymer.

A major problem with SAW is attrition, because of which we are not able to grow large number of long polymer configurations within meaningful computer times. Several algorithms have been proposed and investigated addressing the problem of attrition. These include the True Self Avoiding Walk(TSAW) [4], Kinetic Growth Walk(KGW) [5], Smart Kinetic Walk(SKW) [6], Interacting Oriented Self Avoiding Walk (IOSAW) [7] *etc.*, to name a few. The most recent addition to this list is the Interacting Growth Walk (IGW) proposed by Narasimhan *et al* [8].

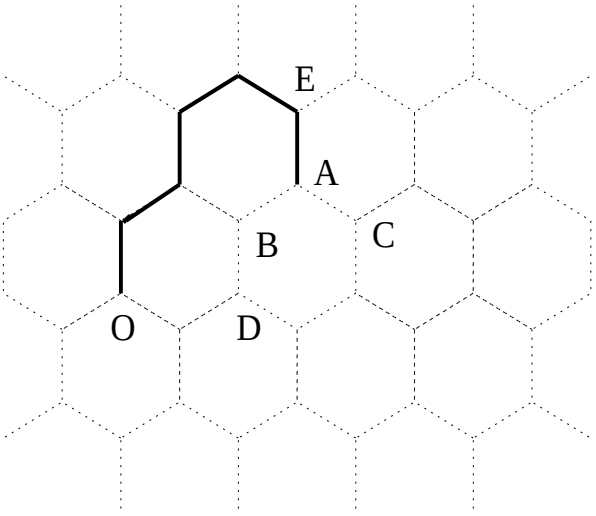

FIG. 1. IGW on a honecomb lattice. The first step from O is taken with a probability 1/3. All the subsequent steps until site A are taken each with a probability 1/2. If the walk at site A goes to site B, then an nbNN contact develops lowering the energy. The probability for this step is $p(A \rightarrow B) = \exp(\beta')/[1+\exp(\beta')]$ On the other hand the step from A to C does not change the energy and $p(A \rightarrow C) = 1/[1+\exp(\beta')]$. If the walk goes from A to B, then it is immediately followed by a step from B to D with unit probability.

In IGW, we define a growth temperature T' that controls locally the growth process as described briefly below. We consider a non reversing and myopic ant rather than a blind ant. The probability of moving to a site that makes, say μ number of nbNN contacts is made proportional to $\exp(\beta'\mu)$. This is illustrated in Fig. 1, where we consider SAW on a honeycomb lattice. A typical SAW trail is marked by thick connected line segments in Fig. 1. For the honeycomb lattice $z = 3$ and $\mu = 0,\ 1$. The walk at site marked A in Fig. 1, can move either to the site B or to the site C. If the site B is selected, the energy would be reduced by one unit since this choice results in an nbNN contact. Hence we choose the site B with a relatively higher probability determined by the growth temperature T': $p(A \rightarrow B) = \exp(\beta')/[1+\exp(\beta')]$. On the other hand, the step from site A to site C, does not lead to any change in the energy, and $p(A \rightarrow C) = 1/[1+\exp(\beta')]$. Note that whenever a contact making site is selected, it is followed immediately by a step to the only remaining nearest neighbour site, and the probability for this is unity. In Fig. 1, if the walk reaches site B then then in its next step it goes to site D with a probability $p(B \rightarrow D) = 1$. Let us say that in an N step SAW, grown as per the myopic ant IGW algorithm, there are n_{NN} contact steps accepted and n'_{NN} contact steps avoided during the growth process. For example in Fig. 1,. if the step A to B is taken then we say the contact is accepted. On the other hand if the step A to C is taken then we say the contact is avoided. We then have,

$$\begin{aligned}\mathcal{P}_N^{\rm IGW}(\beta') = \frac{1}{3}\left(\frac{1}{2}\right)^{N-1-2n_{NN}(\mathcal{C})-n'_{NN}(\mathcal{C})} \\ \times \left[\frac{\exp(\beta')}{1+\exp(\beta')}\right]^{n_{NN}(\mathcal{C})} \\ \times \left[\frac{1}{1+\exp(\beta')}\right]^{n'_{NN}(\mathcal{C})} \qquad (4)\end{aligned}$$

Let us consider two extreme cases.

Case 1 : $\beta' \rightarrow \infty$ ($T' \rightarrow 0$)

For this case $n'_{NN}(\mathcal{C}) = 0\ \forall\ \mathcal{C}$, since whenever a contact making step is available, the random walk takes it with probability unity. In Fig. 1, this corresponds to $p(A \rightarrow B) = 1$ and $p(A \rightarrow C) = 0$. Identifying $E(\mathcal{C}) = -n_{NN}$, we have,

$$\mathcal{P}_N^{\rm IGW}(\beta' = \infty) = \exp\left[-(\ln 4)E(\mathcal{C})\right] \times \frac{1}{3}\left(\frac{1}{2}\right)^{N-1} \qquad (5)$$

We immediately see that the IGW ensemble at growth temperature $T' \rightarrow 0'$ ($\beta' \rightarrow \infty$) corresponds to ISAW ensemble at $k_BT = 1/\ln 4 = 0.7213$ ($\beta = \ln 4$).

Case 2 : $\beta' = 0$ ($T = \infty$)

At very high growth temperatures ($T' \rightarrow \infty$), the nbNN contact interaction is unimportant and the walk steps into one of the unvisited nearest neighbour sites with equal probability. We have,

$$\mathcal{P}_N^{\rm IGW}(\beta' = 0) = \exp\left[-(\ln 2)E(\mathcal{C})\right] \times \frac{1}{3}\left(\frac{1}{2}\right)^{N-1} \qquad (6)$$

Thus at very high growth temperatures ($T' \rightarrow \infty$) ($\beta' \rightarrow = 0$) IGW ensemble is equivalent to ISAW ensemble at $k_BT = 1/\ln 2 = 1.4427$ ($\beta = \ln 2$).

Let us now investigate what happens when $0 < \beta' < \infty$. We rewrite Eq. (4) as,

$$\mathcal{P}_N^{\rm IGW}(\beta') = \exp\left[-\ln\left(F(\beta')\right) E(\mathcal{C})\right] \times \left[\frac{2}{1+\exp(\beta')}\right]^{n'_{NN}(\mathcal{C})} \times \frac{1}{3}\left(\frac{1}{2}\right)^{N-1}, \quad (7)$$

where,

$$F(\beta') = \frac{4\exp(\beta')}{1+\exp(\beta')} \quad (8)$$

The bias arising due to the contact sites avoided during the growth process can be removed by attaching a weight $W(\beta',\ \mathcal{C})$ to a walk $\mathcal{C}$ generated as per the IGW algorithm. It is given by,

$$W(\beta',\mathcal{C}) = \left(\frac{1+\exp(\beta')}{2}\right)^{n'_{NN}(\mathcal{C})} \quad (9)$$

The weighting for the bias removal is implemented as follows. Start an IGW with a weight $W = 1$. Every time a contact is available but not taken by the random walk, multiply the weight by a factor given by $[1+\exp(\beta')]/2$. Let $W(\beta',\mathcal{C})$ be the weight at the end of an N-step walk. Thus the IGW ensemble at β' defined by the set of weights $\{W(\beta',\mathcal{C})\}$ is equivalent to ISAW at $\beta = \ln F(\beta')$, where $F(\beta')$ is given by Eq. (8).

Infact, if we accept a weighted IGW ensemble, we can choose the weights appropriately (called importance sampling [9]) to make a correspondence with ISAW ensemble, such that β' of IGW is the same as β of ISAW. This is carried out as follows. Let,

$$F_1(\beta') = \frac{4}{1+\exp(\beta')}$$
$$F_2(\beta') = \frac{2}{1+\exp(\beta')}. \quad (10)$$

Then we have,

$$\mathcal{P}_N^{\rm IGW}(\beta') = \exp\left[-\beta' E(\mathcal{C})\right] \times \left[F_1(\beta')\right]^{n_{NN}(\mathcal{C})} \times \left[F_2(\beta')\right]^{n'_{NN}(\mathcal{C})} \times \mathcal{P}_N^{\rm SAW}, \quad (11)$$

where $E(\mathcal{C}) = -n_{NN}(\mathcal{C})$ and $\mathcal{P}_N^{\rm SAW}$ is given by Eq. (1) with $z = 3$. The factors which depend on F_1 and F_2 can be taken care of by attaching suitable statistical weights to the configuration. Essentially, we start the random walk with a statistical weight $W = 1$. At any stage of the growth process, if both the nearest neighbour sites are not contact making sites, then we choose one of them with equal probability and proceed. We do not do anything to W. In Fig. 1, when the walk goes from the site E to A, we do not adjust W. On the other hand if the step leads to a contact (the step A to B in Fig. 1), then W is multiplied by $1/F_1(\beta')$. If the step avoids a contact (A to C in Fig. 1), then we multiply W by $1/F_2(\beta')$. Note that these weight adjustments are carried out in the same spirit as the PERM B algorithm proposed by Grassberger [9]. We carry out the above weight multiplication everytime a contact making step or a contact avoiding step is made during the growth process. Let $W(\beta',\mathcal{C})$ be the weight at the end the N step walk $\mathcal{C}$. It is immediately seen that if the IGW is weighted as per the above procedure, then the growth temperature T' is the same as the temperature T of the canonical ensemble of ISAW. Thus we have an IGW ensemble defined by the weights $\{W(\mathcal{C},\beta)\}$. We can employ this ensemble to calculate the macroscopic properties like energy, specific heat (fluctuations in energy), end - to - end distance *etc.*

In conclusion, we have shown that IGW at $\beta' = \infty$ is identically equivalent to ISAW at $\beta = \ln 4$. Also IGW at $\beta' = 0$ is identically equivalent to ISAW at $\beta = \ln 2$. For other values of β' we introduce a weight factor to correct for the bias arising due to the contacts avoided during the growth process and show that the weighted IGW at β' is equivalent to ISAW at β given by $\ln F(\beta')$, where $F(\beta')$ is given Eq. (8). Infact by choosing appropriate weights (importance sampling) for the accepted as well as avoided contacts we can render weighted IGW at β' as equivalent to ISAW at $\beta = \beta'$.

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